Chapter 6

Future Directions and Outlook for Radial Junction Wire Arrays

6.1 An Inexpensive, Flexible, Efficient Solid-State Si Wire Array Solar Cell

6.1.1 Efficiency Projections

Now that the radial junction project has successfully demonstrated the controlled fabrication of highly uniform Si wire arrays from abundant materials in a potentially low-cost, scalable process and shown that the inherent energy-conversion properties of such arrays should enable them to make efficient photovoltaic devices, the next logical direction of this research is to construct a solid-state wire array solar cell and optimize its efficiency. Kayes, et al. from our research group made an initial attempt to produce and test a solid-state wire array solar cell fabricated with Si wires from our VLS growth process.[156] While efficiencies up to 0.87% were observed, this cell did not incorporate numerous advances we have made since that time, including high-quality, in situ p-type doping and larger diameter wires.

Based on modeling,[34] single-wire measurements,[121] absorption studies,[122] and wire array photoelectrochemical measurements (see Chapter 5)[146] on our current Si wires, we expect a well-constructed solid-state cell to have a significantly better performance, with an efficiency > 10% within reach. Solar cell efficiency, η, is determined by:

$$\eta = \frac{J_{sc} V_{oc} f}{P_{in}} \tag{6.1}$$

where J_{sc} is the short-circuit photocurrent density, V_{oc} is the open-circuit voltage, f is the fill factor, and P_{in} is the power density of the incident illumination. The relevant solar cell efficiency is that occurring under the white light of the solar flux at the Earth's surface. This is approximately 100 mW cm^{-2} for AM 1.5 illumination, which has a very similar photon flux to a 60 mW cm^{-2} intensity of 808 nm illumination. Therefore, the uncorrected values from Table 5.1 for a peeled, polymer-supported wire array photoelectrochemical cell at 60 mW cm^{-2} 808 nm illumination can be used in Equation 6.1 with a P_{in} of 100 mW cm^{-2} to estimate an efficiency under white light of ~ 1.1%. This efficiency, though a promising start, could be greatly increased by incorporating improvements achieved in the laboratory on various aspects of the wire array cell design. Increasing the J_{sc} in the cell to 35 mA cm^{-2} by effectively trapping light within the Si wires ($\Phi_{ext} \sim 0.9$) would result in $\eta \sim 5.2\%$.[155] This is a realistic projection considering that up to 96% absorption has been measured at normal incidence with this wire array geometry by including a Lambertian back reflector and an antireflection coating on the wire surfaces. Wires with a clean surface free of catalyst impurities, i.e., from a KOH etch (Figure 5.8) or effective gettering procedure, have demonstrated uncorrected fill

factors ~ 0.55. Combined with effective light trapping, this results in η ~ 8.2%. If the same improvements are made in a solid-state device, such that concentration overpotential and solution resistance losses are eliminated, the fill factor can be corrected to ~ 0.7, leading to η ~ 10.5%. Finally, if this device incorporates good p-n junctions with passivated surfaces, for which single-wire measurements have demonstrated V_{oc} ~ 580 mV, the efficiency could be ~ 14.2% or higher. These projections are reasonable and based on results that have already been achieved through laboratory experiments on these Si wires.

6.1.2 Envisioned Fabrication Process

We have devised a realistic plan for the fabrication of an efficient solid-state wire array photovoltaic device. Figure 6.1 shows a schematic of the envisioned process. As we have previously demonstrated,[119] a Si(111) wafer with a thermally grown SiO_2 buffer layer with patterned islands of Cu catalyst (Figure 6.1a) is used as a substrate to epitaxially grow vertically aligned p-Si wires of controlled length, diameter, spacing and arrangement (Figure 6.1b) from gaseous $SiCl_4$ via the VLS growth mechanism. The Cu catalyst tips are then chemically removed (as in Section 5.2.2), metal impurities are removed by gettering to the feasible limit (possibly by extended immersion in $FeCl_3$ or another Cu etchant), and a thin thermal oxide, ~ 200 – 300 nm, is grown on the surface of the Si wires (Figure 6.1c). The array is infiltrated with a ~ 10 μm thick layer of PDMS at the base of the wires (Figure 6.1d), with the same method used to produce peeled, polymer-supported Si wire arrays (see Section 5.2.2). The oxide shell is then removed

from the exposed wire areas using buffered HF. The PDMS, which masks the underlying oxide from the HF etch, is subsequently removed by > 20 min in a 3:1 dimethylformamide: tetrabutylammonium fluoride etch,[157] leaving the SiO_2 layer intact (Figure 6.1e). This process has been experimentally demonstrated, yielding highly uniform p-Si wire arrays with an oxide sheath on the bottom ~ 10 μm of the wire (Figure 6.2). By casting additional layers of PDMS before the buffered HF etch, the length of this oxide shell can be tuned from 10 μm to the full length of the array.

The surface of the wires is next doped n-type to a depth of ~ 200 nm using a diffusion doping procedure (Figure 6.1f). This has been experimentally achieved by heating Si wire arrays to 850 ºC in the presence of n-type doping wafers (a phosphorus source) under carefully controlled conditions for 10 min. The oxide at the base of the array acts as a diffusion barrier, preventing the bottom of the wires from developing an n-type shell. The thin oxide barrier is therefore critical to enabling a back contact to the p-Si wire cores that does not form shunts through the n-Si shells. The doping process leaves a thin glass phase of high P concentration at the surface of the wires that must be removed. A surface etch and oxide etch treatment is used to remove < 50 nm of the wire surface as well as the oxide shell at the base of the rods (Figure 6.1g). Passivation of the Si wire surfaces could be included at this stage of the fabrication procedure as well. Surface recombination could be mitigated by methyl termination of the Si surface[52, 158] or by the conformal deposition of a thin amorphous Si layer.[21]

With the preparation of the absorber and emitter elements of the Si wires complete, the array is next embedded in a supporting matrix of transparent PDMS (Figure 6.1h).

The PDMS infill allows the wire array to be transferred from the single-crystal growth substrate to a flexible film, permitting the substrate to be recycled for the production of subsequent wire arrays (see Sections 4.2.2 and 4.3). Ideally, the thickness of the PDMS matrix should be precisely controlled and expose only the tips of the wires for an eventual front contact. This can be achieved by depositing the polymer in multiple thin layers (see Section 5.2.2) until the desired thickness is reached. However, uniformly exposing only the tip of the wire from the polymer layer requires that the wires be of identical length across the entire area. In practice, the wires tend to be longer near the edges of a sample and of a more uniform height across the interior area of the substrate. Producing polymer-embedded arrays with only the wire tips exposed could possibly be achieved by growing large areas of Si wire arrays in each growth run (i.e., an entire patterned Si wafer). Alternatively, if height variation across wire arrays is problematic, a planarization step could be added to the process between catalyst removal and growth of the thermal oxide on the wires by an infill with spin-on glass followed by chemomechanical polishing and then a wet chemical etch to remove the spin-on glass.[159] The PDMS infill could additionally be utilized to improve light absorption within the array by including scattering elements within the matrix during polymer deposition. Experiments with well-dispersed particles of alumina of ~ 1 μm diameter in the PDMS layer have shown promise as a way to increase absorption.

After the transfer of the wire array from the growth substrate to a PDMS film, front and back contacts must be applied to complete the solar cell (Figure 6.1i). The back contact should make an ohmic electrical connection between each p-Si core while reflecting light from between the wires back into the array. For the polymer-supported

wire array photoelectrodes of Chapter 5, this was accomplished by thermally evaporating Au onto the back of a freshly peeled film. For scalability and economic viability, the use of rare metals should be minimized (see Figure 3.1). If, however, a metal such as Au is deemed to be necessary for the formation of an ohmic contact on this structure, the amount required could be greatly reduced by plating it on the bottom of the wires by electroless deposition and then interconnecting the wires by evaporation of another more common metal. Ideally though, an Al layer would be evaporated on the back and the film heated at low temperature (< 200 ºC) to form a reflective, ohmic back contact with a single, earth-abundant material.[29] The back surface should be rough enough that the metal acts like a Lambertian reflector, which has been demonstrated to maximize the absorbance in Si wire arrays.[122] The top contact, on the other hand, needs to electrically connect the highly doped n-type emitter shells while being as transparent as possible. A sputtered indium tin oxide (ITO) layer could serve this function, but another transparent conducting oxide with more abundant elements, such as fluorine-doped tin oxide (FTO) or aluminum zinc oxide (AZO), would make the cell more scalable. Unfortunately, these oxides are fairly brittle and would likely crack significantly in a flexible device. If made highly conducting and thin enough, a conductive polymer (i.e., PEDOT: PSS) could potentially be a flexible, transparent top contact to the n^+-Si shell. PDMS has been made conductive (10^{-2} Ω-cm) by the incorporation of Ag nanoparticles into the matrix.[160] By replacement of the Ag with well-dispersed ITO nanoparticles or nanowires,[161] a flexible, transparent, conductive PDMS top contact may be possible. Alternatively, a nontransparent metal could interconnect the n-Si shells at the base of the emitter layer, leaving the majority of the wire length uncovered to absorb light (Figure 6.3). This

contacting scheme could be accomplished by deposition of the metal after embedding the array in a layer of PDMS just thicker than the p-Si wire base, then casting an additional thin PDMS layer, etching any excess metal off the exposed wires, and then fully embedding the rest of the array in supportive polymer before peeling the film and adding a back contact.

The final device would be an inexpensive, flexible, efficient solid-state Si wire array solar cell (Figure 6.4). Once the fabrication of the device is realized, its efficiency would be improved by optimizing the wire diameter and spacing. The optimal geometry would be one that gets the most voltage and photocurrent with the least amount of Si. Further efficiency gains would be sought by improvements in surface passivation and contacting methods.

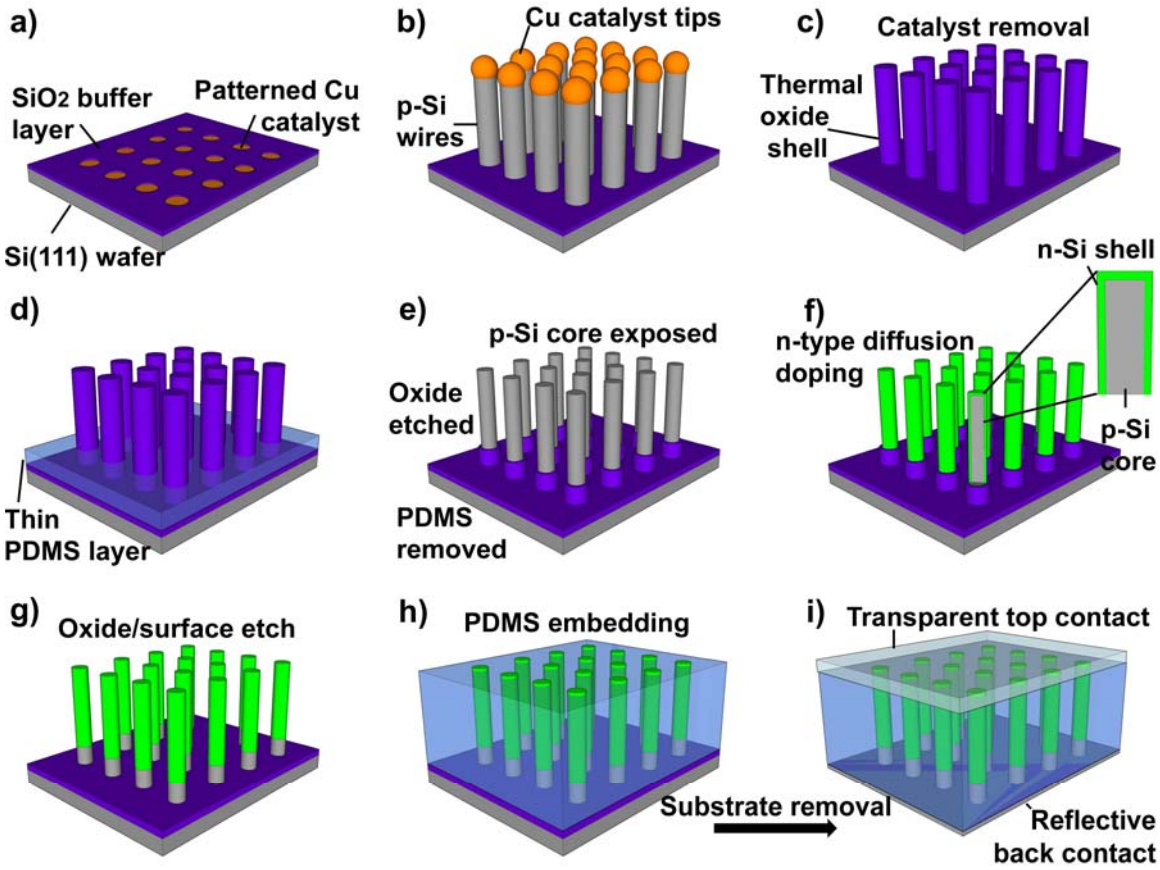

Figure 6.1. Schematic of the envisioned process for producing solid-state Si wire array solar cells. **(a)** A Si(111) wafer with patterned Cu catalyst in a buffered oxide template is used to grow **(b)** vertically aligned, p-Si wires, as previously demonstrated. **(c)** The catalyst tips are chemically removed and then a thermal oxide is grown on the wires. **(d)** A thin PDMS layer is cured at the base of the wires followed by **(e)** an oxide etch step and subsequent chemical removal of the PDMS, leaving an oxide shell at the base of the wires to act as a diffusion barrier. **(f)** A diffusion doping procedure is used to make an n-Si shell on the wire array above the oxide-covered base, and then **(g)** another etch is used to remove the surface layer. **(h)** The wire array is embedded in PDMS, leaving the tops of the wires exposed. **(i)** The PDMS/wire array composite film is removed from the substrate followed by the deposition of a reflective back contact and a transparent top contact.

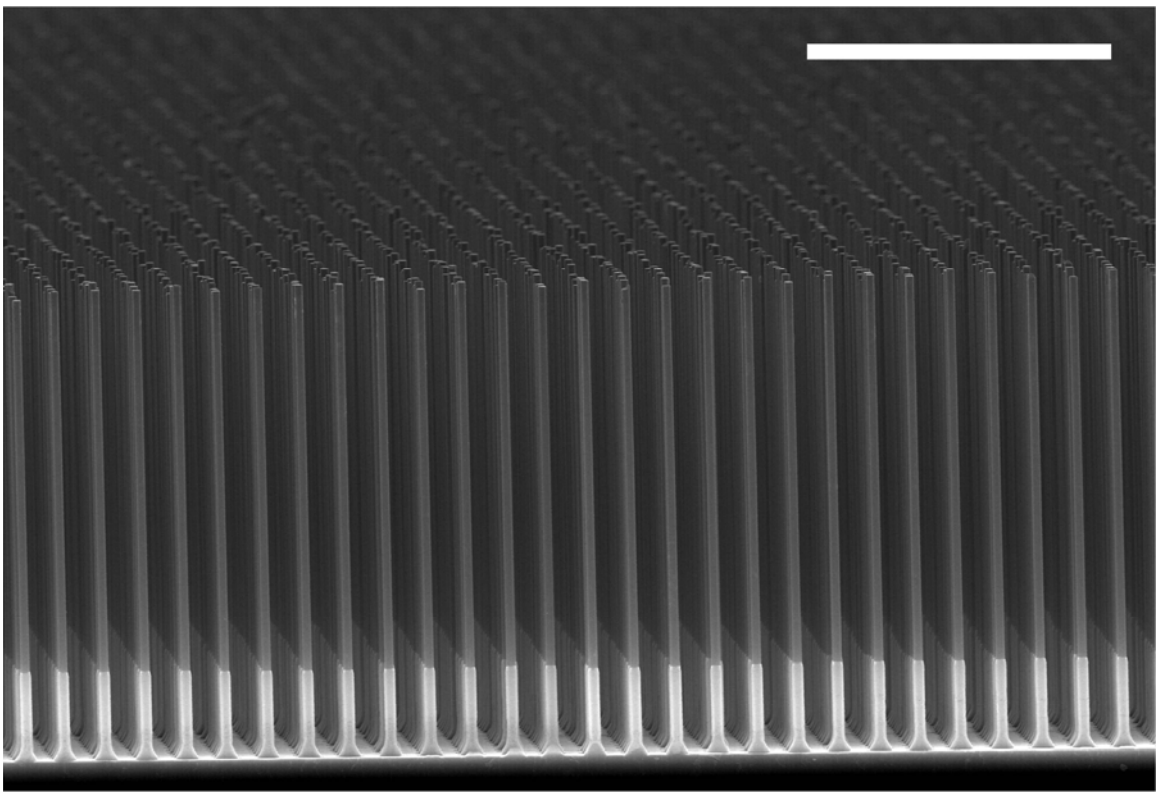

Figure 6.2. Si wire array with an oxide shell on the bases of the wires. Cross-sectional SEM image of an array that had a ~ 300 nm oxide shell thermally grown on the wires, followed by embedding in ~ 10 μm PDMS. The oxide above the PDMS film was etched away in buffered HF, and the PDMS was etched away in 3:1 dimethylformamide: tetrabutylammonium fluoride. Scale bar is 50 μm (image credit: S.W. Boettcher).

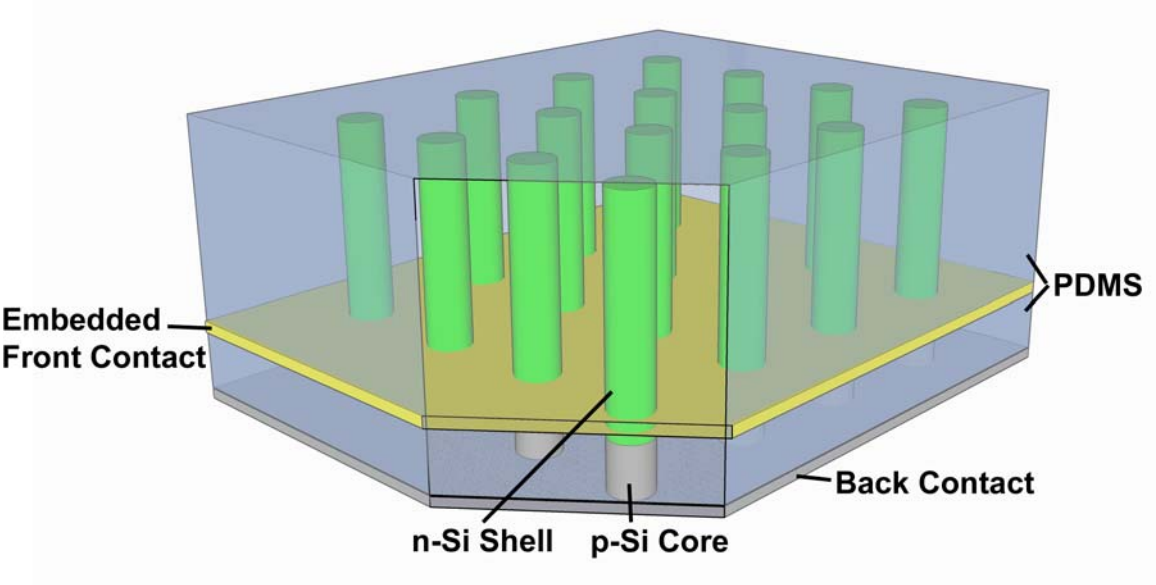

Figure 6.3. Embedded front contact scheme for a solid-state Si wire array solar cell. To avoid the need for a flexible, transparent front contact, a reflective metal could be placed at the bottom of the n-Si emitter layer instead.

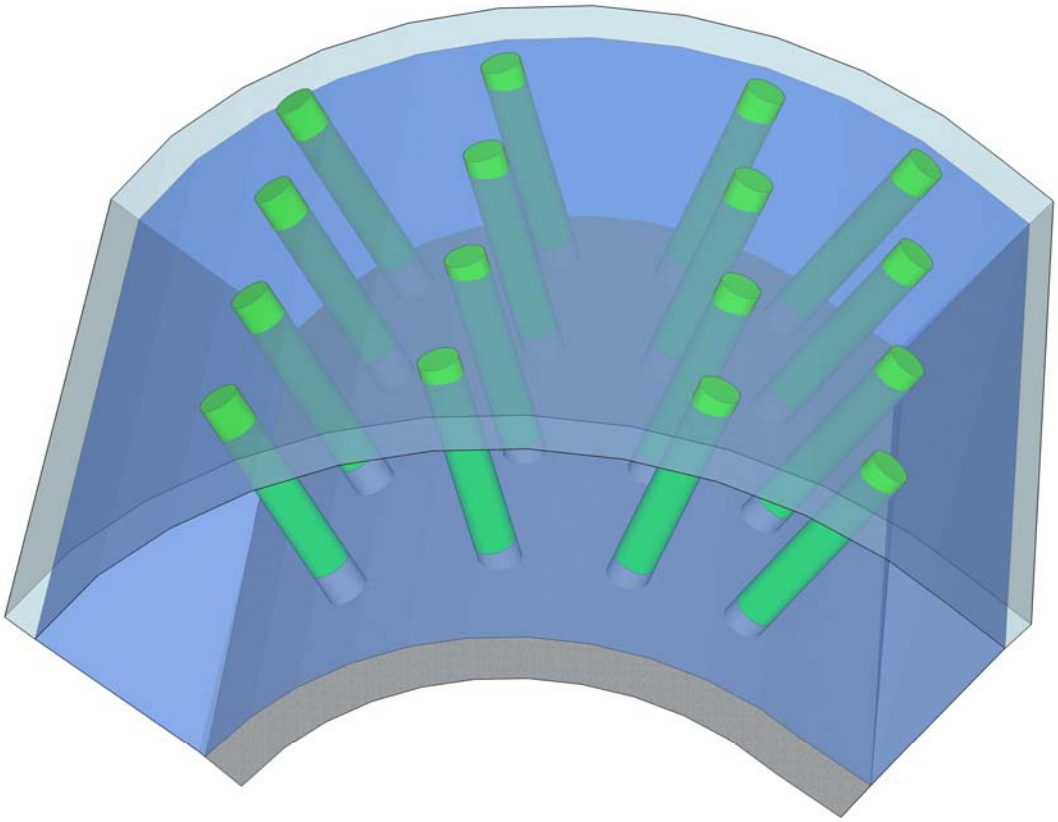

Figure 6.4. Flexible, solid-state Si wire array solar cell. Schematic of a core-shell pn-junction wire array embedded in transparent PDMS with a transparent top contact and reflective back contact. The composite film would have the benefits of a single-crystal inorganic semiconductor and a flexible organic material while using a fraction of the Si required in a planar arrangement.

6.1.3 Cost Comparison to Planar Si

While a thorough cost analysis is beyond the scope of this work and perhaps premature until a definite fabrication route is selected, some speculation of the manufacturing cost of the wire array solar cell compared to current planar Si technology can be made. Referring back to Figure 1.4, it is likely that the Si wire array solar cell could see significant cost savings in the areas of feedstock, ingot growth, and wafering. The primary feedstock for the wire array process is $SiCl_4$, an inexpensive chlorosilane that is

currently an unwanted byproduct. Rather than the growth of high-purity ingots, these wire arrays are grown with Cu catalyst, a fairly abundant metal, at atmospheric pressure without rigorous purification steps. The growth process is still fairly high temperature, but growth rates are high, too. Moreover, wafering expenses should be dramatically reduced as there are no kerf losses and a significantly lower volume of Si is required per cell area for wire array photovoltaics. It is unclear how cell processing costs would compare, as the wire array cell still involves high temperature doping and the integration of top and bottom contacts. The PDMS embedding steps should be low-cost because they involve an inexpensive polymer that could be applied in a roll-to-roll process. The substrate recycling procedure, although it adds some complexity, should greatly reduce the expense associated with using a single-crystal wafer. Module assembly costs would likely be comparable, except that as a flexible photovoltaic that could be rolled out, the wire array cell would not need expensive framing or glass. Finally, the balance-of-systems costs would likely be reduced as well. Although some increase in expense is possible in the wire array case because these cells would probably be somewhat lower in efficiency and would therefore need to cover a larger area to produce the same amount of energy, that cost would be offset by the significantly easier process required to install a system of lightweight, flexible wire array cells relative to a heavy, brittle crystalline system. Overall, the wire array solar cell design has the potential to substantially reduce the cost of manufacturing Si-based photovoltaics.

6.2 A Solar Water-Splitting Membrane Using Earth-Abundant Semiconductors in Radial Junctions

6.2.1 Water-Splitting Membrane Concept

Even if a revolution in the manufacture of photovoltaics successfully reduces the cost of solar electricity to a level that is economically competitive with fossil fuels, the widespread implementation of solar as a primary energy source will require the ability to overcome the diurnal variation of sunlight in a given region. In order to have energy from the sun at night, a cost-effective storage mechanism is needed. The use of batteries to store electricity could work in principle, but all current battery technologies are too expensive. Mechanical storage methods, such as pumping water uphill or compressing gases, are a possibility, but this approach would require enormous reservoirs to be filled and emptied everyday (i.e., a pumping capacity of > 5000 Hoover Dams to meet U.S. energy demand).[11] The ideal solution would be to store solar energy in the form of chemical bonds – to convert sunlight into an energy-dense fuel. Nature utilizes this approach through the mechanism of photosynthesis. However, the energy conversion and storage efficiency of even the most rapidly growing plant is < 0.5%.[11] Higher efficiencies should be possible in an artificial photosynthesis device that does not divert energy to rebuild complicated biological systems as a plant must do. For instance, solar photoelectrolysis has been demonstrated at conversion efficiencies up to 18.3% using AlGaAs/Si bipolar band gap cells with RuO_2 and Pt catalysts.[162, 163] Unfortunately, this cell is far too expensive to be a practical energy storage solution. Combining electrolyzers directly with photovoltaics has not been cost-effective on a large scale either

due to the need for wires and expensive catalysts. Instead, a scalably manufacturable device using only earth-abundant elements is needed that is significantly more efficient than plants at generating fuel from sunlight.

We have developed a credible scheme to accomplish this goal by building a water-splitting membrane that uses the advantages of radial junctions. Figure 6.5 demonstrates how this membrane would work. The electrolysis of water into hydrogen and oxygen thermodynamically requires 1.23 V, with overpotential losses driving the necessary potential even higher. To split water directly from the photovoltage of a semiconductor, there is an additional requirement that the conduction and valence band energy levels must straddle the oxidation and reduction potentials of the electrolysis reaction. Meeting these requirements while simultaneously being efficient, stable, and earth-abundant is a lot to expect from a single material. No known semiconductor currently satisfies all of these criteria effectively. The proposed membrane would therefore use two separate materials in series to build the photovoltage needed to split water. Rather than relying on one very wide band gap material that could only use UV light, the device would make more efficient use of the solar spectrum by employing a wider band gap photoanode material that would absorb higher energy light while transmitting lower energy light to be absorbed by a narrower band gap photocathode material. The two semiconductors would be electrically connected to each other through an ion exchange membrane that would be impermeable to hydrogen and oxygen gases while allowing the transfer of protons. The ion exchange function is necessary to prevent the buildup of a pH gradient. Both semiconductors would be in the form of wire arrays, with the radius tuned to the minority-carrier collection length of the material and the length adjusted for optimal light

absorption. The spacing of the wires would be optimized for the tradeoff between optical absorption and mass transport (i.e., bubble formation and the removal of gaseous products from the array). The wire surfaces would be decorated with bonded multi-electron transfer catalysts to drive the oxidation and reduction reactions at low overpotentials. By shaping the semiconductors as wire arrays, lower-purity materials can be used and spaces are created for ion transfer across the membrane. Furthermore, charge-carriers will be distributed over a larger area, reducing the turnover frequency at catalyst sites and lowering the necessary activity of those catalysts. This will allow more earth-abundant materials to be candidates for the catalysis of the reaction. The product gases would be collected, with oxygen vented to the atmosphere and hydrogen collected for use as a fuel.

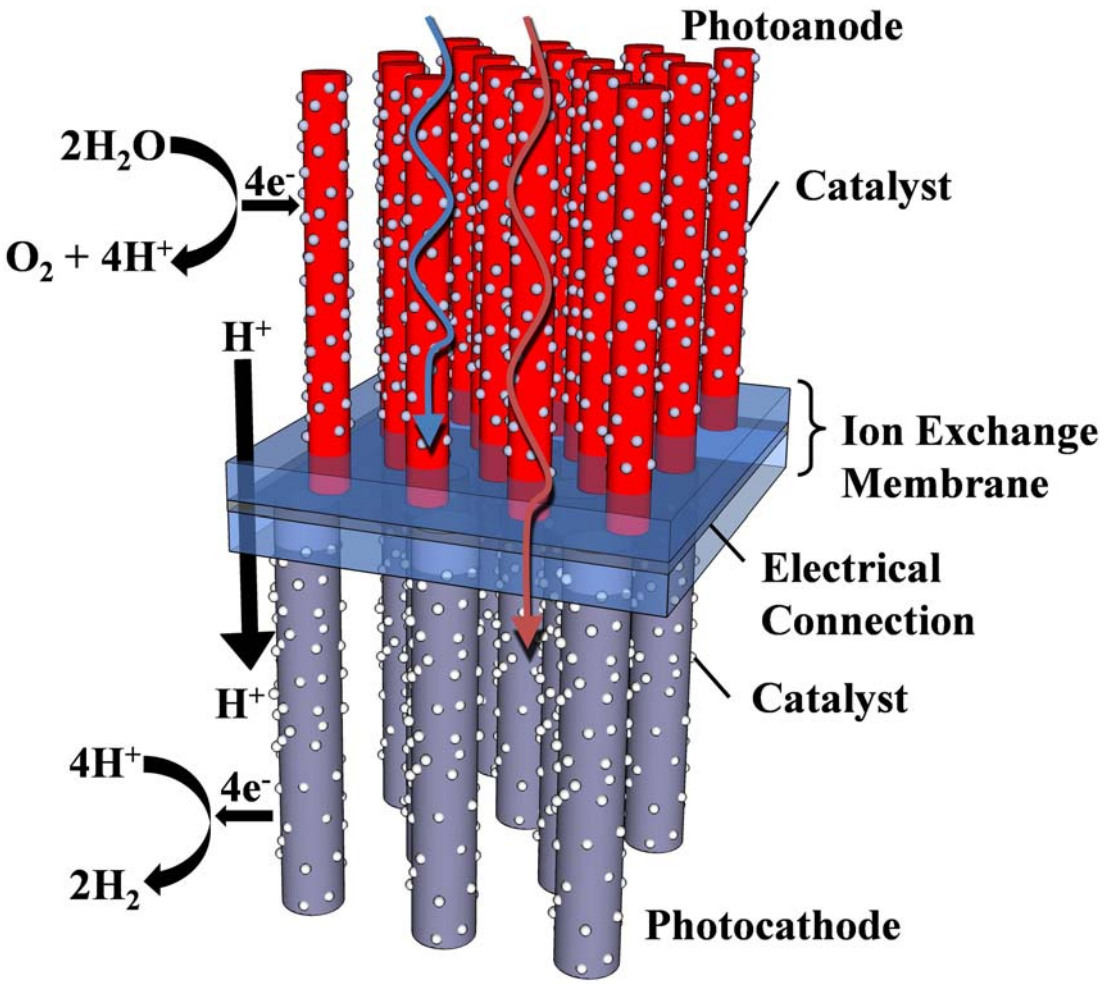

Figure 6.5. Schematic of a water-splitting device to generate fuel from sunlight. The device uses two different semiconductors, a wider band gap anode material and a narrower band gap cathode material, to produce the > 1.23 V necessary to electrolyze water. The anode material absorbs higher energy light, allowing lower energy light to be absorbed by the cathode. The two semiconductors are electrically connected in a transparent membrane that is impermeable to H_2 and O_2 but allows proton transfer. The semiconductors are radial junction arrays in order to utilize lower-purity materials, to distribute charge-carriers over a larger area so that the catalyst turnover requirement is lower, and to allow proton transfer across the membrane. H_2 is collected on the cathode side and O_2 is vented to the atmosphere from the anode side. The image is not to scale.

6.2.2 Photocathode

The photocathode material must be stable under the reducing environment on its side of the cell and have a conduction band edge energy sufficiently negative of the formal potential to produce hydrogen from water in order to make the reaction energetically favorable. One material that could fulfill this role is p-type Si, which is cathodically stable under illumination in aqueous conditions,[164] has its conduction band edge well-positioned relative to the reduction potential to produce hydrogen, and can be coupled to effective catalysts. The work report herein on Si wire arrays (Chapters 3-5) is thus directly applicable to producing a photocathode for this solar fuel generating membrane. Although Pt is the most active catalyst for H_2 production currently known, other earth-abundant metals such as Ni or Co may be effective on these arrays due to the lower flux of charge-carriers through a given area relative to a planar surface. These metals have already been demonstrated as catalysts for hydrogen evolution in conjunction with p-Si.[165]

6.2.3 Photoanode

The photoanode material must be stable under the oxidizing environment on its side of the cell and have a valence band edge energy sufficiently positive of the water oxidation potential to make the reaction energetically favorable. With these criteria, metal oxide semiconductors are favorable because their valence band edges are normally quite positive of the water oxidation potential and because the metal atoms are already in their highest oxidation state. The drawback of many metal oxides is that their band gaps are

too large (> 3 eV) to make efficient use of the solar spectrum and their minority-carrier diffusion lengths are too low for efficient charge-carrier collection.

Although the search for a metal oxide of ideal properties is ongoing, WO_3 is a promising candidate to meet the requirements of the photoanode material. It has a band gap that can absorb much of the visible spectrum (E_g = 2.6 eV)[65] and can be tuned lower by the addition of other metals such as Mo.[166, 167] The minority-carrier diffusion length of WO_3 (up to 10^{-6} m),[168] though short, is longer than most other metal oxide candidate materials for the photoanode. By utilizing WO_3 in a radial junction structure, efficient charge-carrier collection should be possible.

Nanostructured WO_3 for the photoanode could be fabricated by several routes. The most straightforward method to produce wire arrays would be to employ templating techniques, such as the AAO approach described earlier (see Section 2.2.1). W metal could be cathodically electrodeposited and oxidized after removal of the template, or WO_3 (with a Mo fraction) could be electrodeposited into the template directly.[166, 167] In the latter case, a wet chemical etch would be needed that would selectively dissolve the alumina template but not the metal oxide semiconductor rods. Alternatively, a porous film of WO_3, the inverse of a wire array, would accomplish the same task provided that it allowed for sufficient mass transport and transmittance of light to the photocathode (Figure 6.6). Porous WO_3 can be made from the anodization of tungsten foil in a process similar to the fabrication of AAO templates.[169]

Whether the photoanode is a wire array or a porous film, it will need to be decorated with oxygen-evolving catalyst. Finding an earth-abundant catalyst that drives the oxidation of water at low overpotential is one of the largest challenges inherent in the

water-splitting membrane design. Initial research would focus on Co_3O_4 colloids, which are known to be fairly active and stable water oxidation electrocatalysts.[170]

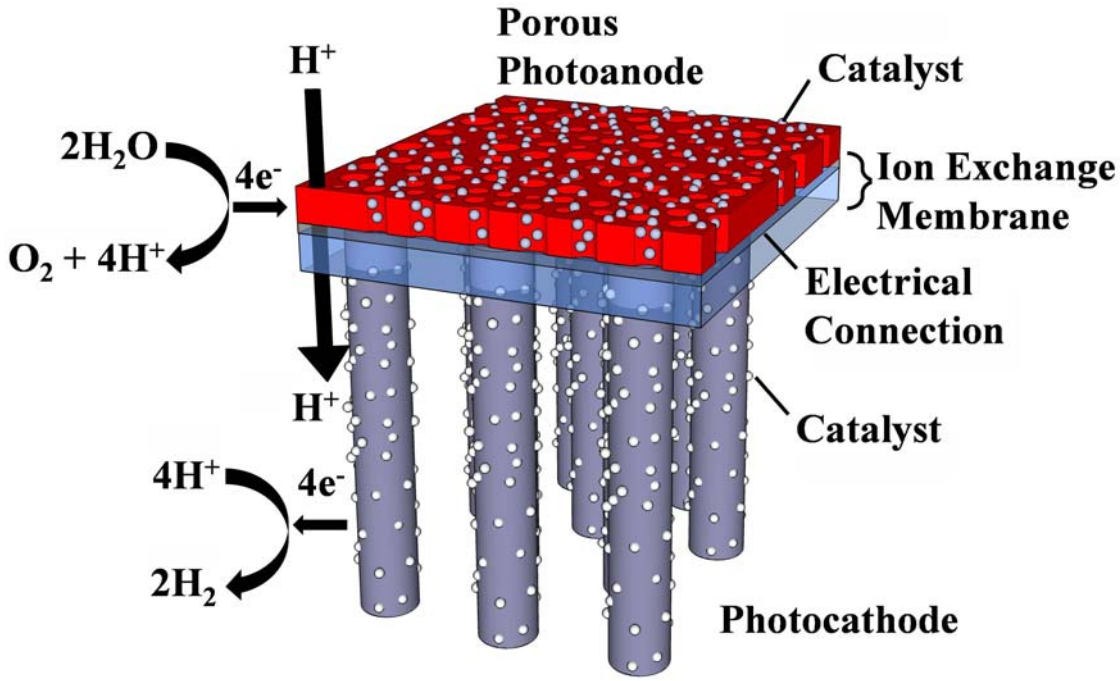

Figure 6.6. Schematic of a water-splitting device using a porous film as a photoanode. While the initial photocathode candidate material, p-Si, can now readily be fabricated into wire arrays of tunable dimensions, the initial photoanode material, WO_3, has not been explored as heavily. Porous anodic WO_3 films could be used as an alternative to metal oxide wires provided that they could be readily incorporated into the membrane device in a way that allowed for sufficient mass transport and transmittance of light to the photocathode.

6.2.4 Membrane and Device Assembly

The membrane layer between the two semiconductor electrodes must fulfill a number of important functions for the device to split water sustainably. It must simultaneously provide structural support for the wire arrays, separate the gaseous hydrogen and oxygen products, enable an ohmic conduction path for electrons between the anode and cathode,

and act as an ion-exchange medium for the protons involved in the electrochemical reaction, all while being optically transparent enough to ensure that light is effectively absorbed by both semiconductor assemblies. There are several approaches that will be explored to meet this daunting challenge.

In its essential functions, the envisioned water-splitting membrane acts as a proton exchange membrane (PEM) fuel cell operating in reverse. The membrane of PEM fuel cells must also be impermeable to hydrogen and oxygen gases while allowing efficient proton exchange. The material most commonly used in these membranes is perfluorosulphonic acid polytetrafluoroethylene copolymer, known as Nafion.[171] Fortunately, Nafion is commercially available and highly transparent when cast from solution. To test the possibility of using Nafion directly as the ion-exchange membrane for the water-splitting device, it was spin-coated from a solution (5% w/w Nafion/alcohol mixture, Alfa Aesar) onto a Si wire array, left to dry for > 2 hr, and then peeled from the substrate using a razor blade. Figure 6.7 shows the resulting Si wire array/Nafion composite film. Although the casting and peeling procedure with Nafion is still unoptimized, a Si wire array with the majority of the wire length exposed can be peeled in a structurally supportive thin film. The thin Nafion layer is not as robust as equivalent PDMS films, but the Nafion does appear to make intimate contact with the wires (Figure 6.7d). To make the full device, each wire array would be peeled in a Nafion film, thin layers of an appropriate metal would be electrolessly deposited on the back of the wire bases to establish an ohmic contact, and the two sides of the membrane would be carefully sealed together using a third, electrically conducting Nafion layer. The middle layer of Nafion would be made conducting by the addition of conjugated polymer chains

or Ag nanoparticles to the extent permitted without substantial degradation of the transparency or ion-exchange capability of this thin film. Well-dispersed nanoparticles may even be beneficial as light scatterers. Alternatively, Nafion or a similar ion-exchange material could be applied by layer-by-layer deposition methods, utilizing the capabilities of that technology to make the material connecting the wire arrays conductive.[172]

In the event that a single material to accomplish the membrane's functions becomes infeasible, a combination of several materials could be used instead (Figure 6.8). In this multi-component membrane, the wires would be peeled from their growth substrates in a structurally supportive polymer to make the water-splitting device mechanically robust. PDMS, as it has already been demonstrated with Si wires (see Section 4.2.2), would be ideal to fulfill this role, although the surface would need to be functionalized to make it hydrophilic and thus permit the aqueous medium to penetrate the array. The two peeled wire arrays would be connected by a layer of conductive polymer (i.e., PEDOT, polypyrrole, etc.), thin enough to be transparent and polymerized or cured between the PDMS layers to adhere them together. Finally, the ion-exchange capability would be provided by Nafion or a similar polymer interspersed throughout the membrane as proton-conducting channels. This structure could possibly be fabricated by selectively removing areas of the membrane with reactive ion etching through a shadow mask, followed by polymer deposition into the resulting pores.

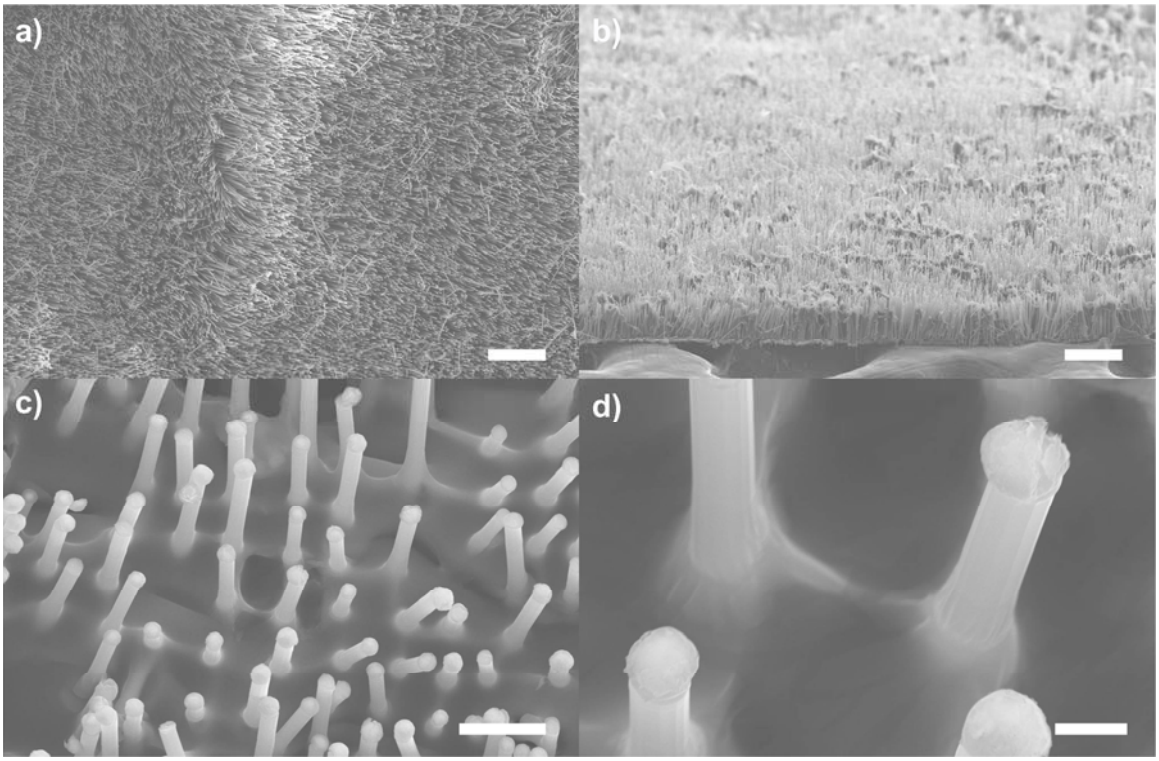

Figure 6.7. Si wire arrays embedded in thin Nafion films. The array **(a)** was uniform over a large area, **(b)** could be peeled from the substrate in a thin polymer film, **(c)** had most of the wire length exposed from the Nafion, and **(d)** made intimate contact with the polymer. Scale bar is 100 μm for **(a,b)**, 20 μm for **(c)**, and 2 μm for **(d)**.

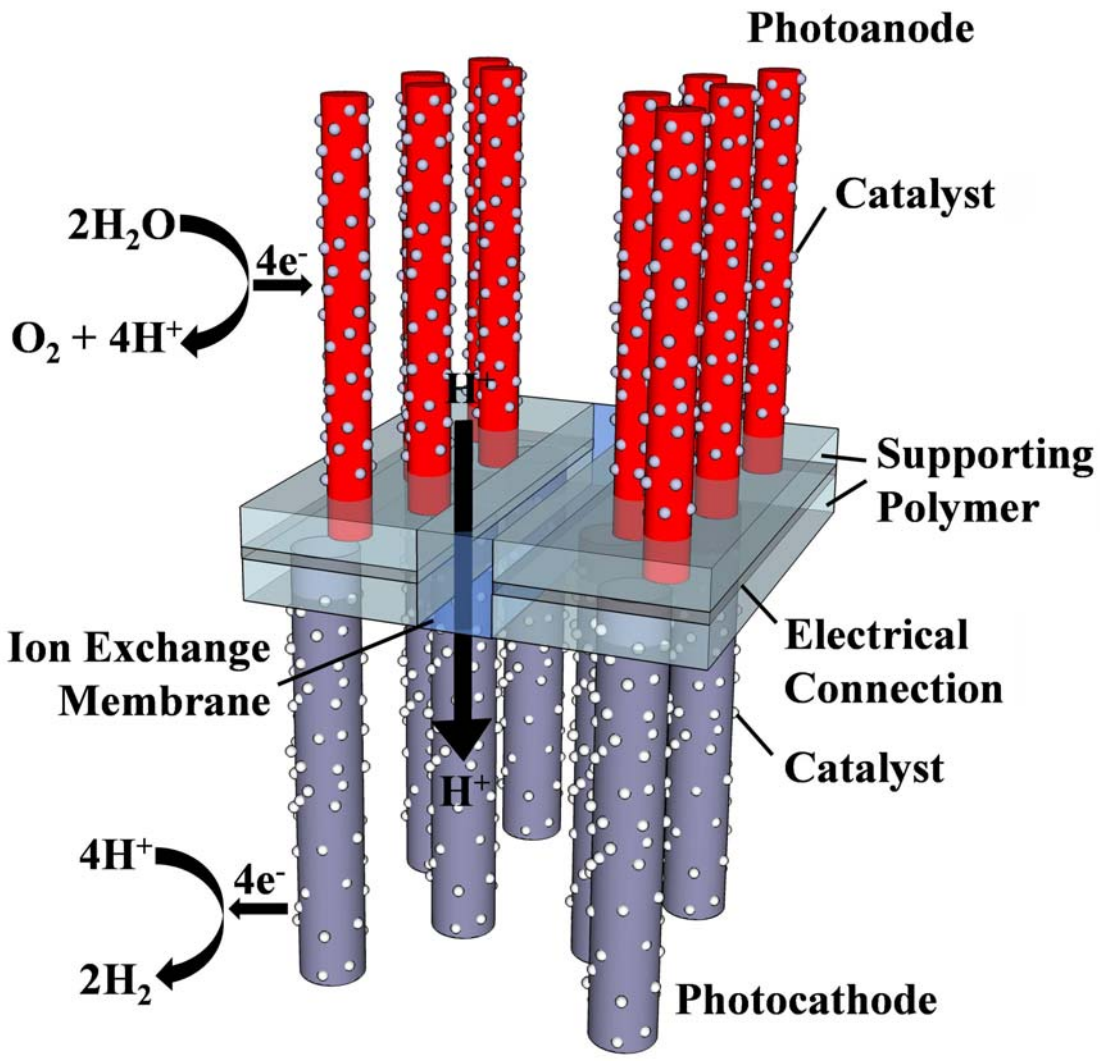

Figure 6.8. Schematic of a water-splitting device using a multi-component membrane. In this version of the device, the membrane is composed of three separate polymers serving three different functions. A structurally supportive polymer at the base of the semiconductor wires gives the device mechanical stability while a conducting polymer provides the electrical connection between the electrodes. A third polymer, interspersed in regions throughout the membrane, allows ion-exchange to occur.

6.2.5 Design Modularity

One of the greatest advantages of the design of this device, from a developmental point of view, is its modularity. Individual components, such as the anode, cathode, membrane, and catalysts, can be studied and improved independently of each other. This added degree of freedom allows multiple researchers to work on different aspects of the device simultaneously, greatly accelerating its development. While the final design of the device may change as improvements and discoveries are made, we expect that the end water-splitting membrane will resemble the image shown in Figure 6.9. The success of this device, which would store sunlight as a chemical fuel, would be a large step towards making solar a viable primary energy source.

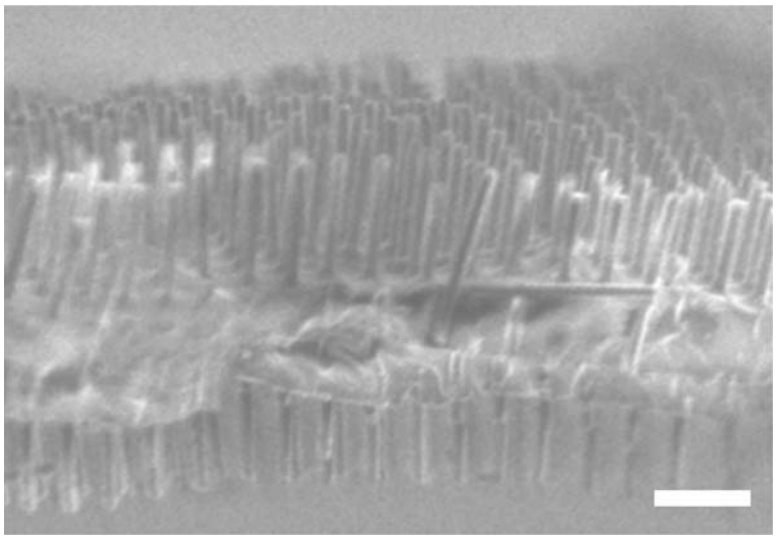

Figure 6.9. Back-to-back polymer-supported semiconductor wire arrays for a sunlight-driven fuel-generating system. Cross-sectional SEM image of two PDMS-supported Si wire arrays adhered to each other. A final water-splitting device with two semiconductor wire arrays in an ion-exchange membrane may resemble this structure. Scale bar is 20 μm.

6.3 Thesis Summary

This thesis has summarized our findings over the last several years fabricating and studying wire array solar cells. The radial junction project has progressed a long way since its inception. Based on our experience and successes to date, we believe it can go much further still.

In the introductory chapter, we explored the global energy situation and how it relates to the ongoing climate change threat. We then evaluated the available carbon-free energy sources and concluded that solar energy must play a vital role in displacing fossil fuels. A cost breakdown of the dominant photovoltaic technology was provided, followed by an explanation of the radial junction concept and how it could potentially lead to less expensive solar cells primarily by reducing feedstock and materials costs. We also discussed the results of modeling on radial junctions, as well as potential ways to fabricate such semiconductor structures and an overview of work that has already been reported on them.

In Chapter 2, we demonstrated the fabrication of Cd(Se, Te) nanorod arrays and compared their photoelectrochemical behavior to analogously produced planar cells. Among the key findings was that the nanorod array open-circuit voltage was significantly lower than that of the planar electrode due to the increased junction area of the device and the increased effects of surface recombination. Nanorod arrays exhibited reduced short-circuit current density as a result of a lower optical filling fraction but generally displayed better fill factors than the planar electrodes. Importantly, spectral response studies demonstrated that nanorod arrays were able to maintain their carrier-collection efficiency

better than planar cells at lower energy, more deeply penetrating wavelengths of light. This observation indicated that the radial junction was allowing better charge-carrier collection at a low minority-carrier diffusion length.

In Chapter 3, we explained why Si would be an ideal candidate for improvement through an architecture employing radial junctions. We discussed the evolution of our approach for the fabrication of controllable, uniform Si wire arrays. Attempts were made to control the dimensions of Si wires by confining them within porous alumina templates during growth. As the need for larger diameter wires became more apparent, wires were increasingly grown by the VLS method without confinement on an epitaxial growth substrate. Better control and growth rates were eventually achieved by switching from SiH_4 to a $SiCl_4$ gas precursor at higher temperatures in conjunction with a lithographically patterned thermal oxide buffer layer on the substrate surface. We demonstrated that uniform Si wire arrays of tunable diameter, length, and spacing could be grown this way from several different catalyst metals. We also demonstrated a general approach using the electrodeposition of catalyst to produce larger diameter, more densely packed wire arrays.

In Chapter 4, we addressed the paradox of using single-crystal growth wafers to fabricate lower-purity Si wire arrays. A scheme was demonstrated to transfer the wire arrays to low-cost polymer films and then recycle the growth substrate for the production of subsequent wire arrays. PDMS-embedded Si wire films maintained the long-range order and alignment of the array while being both durable and flexible. Initial

experimental attempts to densify the wire pattern within the polymer after its removal from the substrate resulted in some success but still require further development.

In Chapter 5, we studied the photoelectrochemical energy-conversion properties of peeled, polymer-supported p-Si wire arrays and compared them to p-Si wire arrays still epitaxially attached to the growth substrate as well as to p-Si planar wafers. The performance of polymer-supported wire arrays was found to be comparable to substrate-attached arrays, both of which displayed better energy-conversion properties than previously reported Si wire array solar cells. Compared to substrate-attached arrays, polymer-supported arrays had similar open-circuit voltages, better fill factors, and slightly lower external quantum efficiencies due to the partial coverage of the wire surface with polymer. All Si wire arrays measured had external quantum efficiencies several times higher than their packing fraction, indicating light trapping and optical concentration within the wires in agreement with previous absorption studies. Furthermore, we showed that high currents within wire arrays should be possible by increasing light absorption, as evidenced by increased external quantum efficiencies (> 0.6) at high angles of incidence.

In this concluding chapter, we discussed two major directions of future research for semiconductors with wire array geometries. The first is to produce an efficient solid-state Si wire array solar cell, which is a logical extension of the work on Si wire arrays presented herein. We described in detail a plan for the fabrication of a solid-state solar cell that should be flexible and reasonably efficient and discussed how the cost of its manufacture would likely compare to current planar Si technology. Because of

significant savings over planar Si in the areas of feedstock, ingot growth, and wafering, this solar cell, if efficient enough, has the potential to be significantly less expensive. We continued by discussing the application for semiconductor wire arrays in a sunlight-driven, water-splitting membrane for the production of chemical fuel. Wire arrays, at both the anode and cathode of this device, would enable the use of low minority-carrier diffusion length materials and possibly allow earth-abundant catalysts by spreading the charge-carriers over a larger area, thereby lowering the activity requirement at catalyst sites. The successful, sustainable operation of a solar fuel-generating membrane would provide an energy-dense storage mechanism for sunlight, which is critical to deploying the solar resource as a primary energy source for the planet.

This thesis has demonstrated that it is possible to fabricate semiconductor wire arrays in a potentially high-throughput, low-cost method that results in an inorganic material in a flexible film form without sacrificing the electronic quality of the material. The primary future direction of this research is to integrate these Si wire array/PDMS composite films into a solid-state solar cell and optimize its efficiency. Advancements in the device will be possible through improving contacts, increasing the voltage by using larger diameter wires with passivated surfaces, ensuring high fill factors by eliminating surface impurities and shunts, and maximizing light absorption with an optimal packing density, a back reflector, and an antireflection layer. If experimental efficiencies in the range of theoretical predictions can be achieved, this technology could have an enormous impact on the photovoltaics market.